In situ threshold photoemission yields correlated to surface reconstructions of InAs (001)

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Threshold photoemission yields for As and In terminated reconstructions of InAs (001) are measured *in situ* and the variation of the photoyield is correlated with the surface stoichiometry. A significant excess in the measured photoelectron yield is found for the In terminated surfaces. These results are compared to a semiempirical model based on density-functional theory calculations of the surface local densities of states for the As terminated $\beta 2$-(2×4) and newly predicted ζ-(4×2) reconstructions. The calculations are in good agreement with the measured trends, and provide a basis for the interpretation of threshold photoemission sensor signatures. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1406552]

Interface morphology, and its variation as a function of growth conditions, is difficult to both identify and control during growth as there are no truly *in situ* sensors, which measure morphology directly. However, nanoscale devices can be dominated by interface properties, such that morphology variation can be a real limitation to achieving reproducible performance among discrete devices. Morphology information may be contained within sensor signatures, but a model of some sophistication must be applied to extract this information. Reflection high-energy electron diffraction (RHEED) and the associated monolayer period oscillations observed during growth are the most accepted example of this principle for molecular beam epitaxial (MBE) growth.[1,2] However, experimental implementation of this technique for the growth of real semiconductor device layers is complicated by the necessity to rotate the substrate during growth. *In situ* optical techniques have the potential to provide both structural symmetry (through polarization) and chemical information. For instance, reflectance difference spectroscopy[3] and second harmonic generation[4] are very surface sensitive techniques, but are also difficult to implement on a growth system where the substrate is rotating.

In this letter we have used threshold photoemission (PE) as an *in situ* monitor of surface morphology during the growth of III–V semiconductor layers by MBE. We have previously applied the threshold PE oscillation technique to monitor and control barrier thicknesses of resonant tunneling diodes used for high speed logic circuits with submonolayer thickness resolution.[5] This work extends our ability to interpret photoelectron yield changes that are superimposed upon the oscillations in terms of chemical stoichiometry and reconstruction variations that can drive the evolution of growth morphology. To assist us in this interpretation, we have developed a semiempirical model of the photoemission process which can be used to characterize and correlate the PE signature.

Experiments were performed in a V80 III–V MBE chamber equipped with In, Ga, and Al effusion cells and EPI valved As and Sb cracking cells. Temperatures were monitored by a thermocouple calibrated against an optical pyrometer. Group III growth oscillations and group V uptake oscillations were measured by RHEED or PE for each substrate temperature,[6] in order to determine the respective fluxes and consequently the V/III ratio.

Photoyields were measured using both broadband and wavelength selective sources. The apparatus for the broadband measurement has been described in detail elsewhere.[7] The wavelength selective configuration incorporated a 150 W D_2 lamp which was focused by an input optic on the entrance slit of an Acton Research vacuum ultraviolet monochromator, allowing wavelength discrimination of the source with an ultimate resolution of 0.01 eV. Photoelectron yields were measured in angle and energy integrated mode in all cases.

Following oxide desorption of the InAs (001) substrates a buffer layer of ~ 0.5 μm thickness was deposited before the surface was sufficiently smooth that growth oscillations could be observed. Typically, observation of RHEED oscillations was a necessary but insufficient criterion for the observation of PE oscillations in broadband mode due to the macroscopically larger sampling area of the PE (~ 1 cm^2) versus RHEED (<1 mm^2) beams.

In Fig. 1 the change in the PE signal level measured from a static surface with a broadband source is shown following the termination of the As_2 flux to the surface at a constant temperature of 470 °C. The development of intensity of the RHEED fourth-order feature in the [1 1 0] azimuth is also plotted in Fig. 1. The continuous change in the measured photoyield is accompanied by surface reconstruction changes, beginning with an As stabilized (2×4) and transitioning to an In stabilized (4×2) reconstruction, as confirmed by the simultaneous RHEED measurements. Systematic variations of the average photoyield have also been ob-

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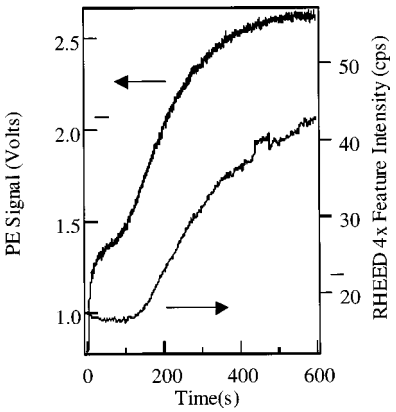

FIG. 1. Measured PE yield and RHEED fourth-order spot from InAs (001) at 470 °C after termination of the As_2 flux.

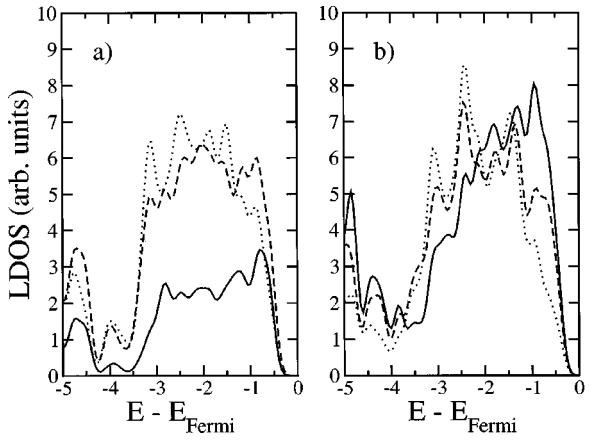

FIG. 2. Calculated LDOS for the first three layers of InAs (001) reconstructions; solid lines are surface layer, dashed lines are second layer, dotted line is third layer. (a) β_2-(2×4), (b) ζ-(4×2).

served with broadband measurements during growth, as a consequence of varying the V/III ratio. Recent scanning tunneling microscopy data and complimentary density functional theory (DFT) calculations[8–10] have shown that the dominant InAs (001) surface reconstruction is observed to change, as a function of decreasing As pressure, from β_2-(2×4), consisting of two on top As dimers and one As dimer in the trench, to α_2-(2×4), having only one on top As dimer and one As dimer in the trench. For very low As_2 flux a (4×2) reconstruction is observed in RHEED and STM for which the exact structure is not known. Recently, it has been predicted that the unusual ζ-(4×2) structure is thermodynamically stable for both GaAs (001)[10,11] and InAs (001).[10] Our own calculations for InAs (001) also indicate that the ζ-(4×2) structure is in fact lower in energy than the β_2-(4×2), previously thought to represent the lowest energy In rich surface structure.[9] The initial As_2 flux of Fig. 1 corresponds to conditions required to produce a β_2-(2×4) reconstruction as measured by STM analysis and the inflection point of the photoyield curve, observed 100 s after termination of the As_2 flux, corresponds to a condition where RHEED indicates the development of a metal-rich reconstruction. This behavior clearly shows that the average photoyield is sensitive to the surface stoichiometry, and in particular, to the coverage of As_2 dimers on the surface. More generally, the average photoyield is sensitive to the relative coverage of empty versus filled dangling bond surface states. This conclusion is supported by a comparison of our calculated photoyield from the ζ-(4×2) and the β_2-(4×2) In terminated surfaces, neither of which have surface As_2 dimers, and both of which show enhanced photoyield with respect to the β_2-(2×4).

The change in the photoemission yield with reconstruction can be explained by considering the surface electronic structure. We have constructed a semiempirical model of the *in situ* photoemission sensor based upon *ab initio* density functional theory (DFT) calculations of the surface local density of states (SLDOS). We describe the photoelectron yield using a simplified form of the three step approximation,[12] in which the primary dependence of $Y(\omega)$ is on the initial z-dependent local density of states

$$Y(\omega)=A(\omega)\int_{E_{\mathrm{vac}}-\hbar\omega}^{E_{\mathrm{fermi}}} dE_i \int_{-\infty}^{0} dz\, D(E_i,z)e^{-z/\lambda},$$

where $A(\omega)$ represents the lamp spectrum and $D(E_i,z)$ is the z-dependent local density of states. We have assumed a constant matrix element between initial and final states since we perform both angle and energy integration of the final state.[13] The final density of states $D(E_f,z)$ is assumed to be dominated by the continuum of outgoing states, which are evanescent (exponentially damped) in the surface layer of the crystal. We treat the combined final density of states and escape probability[12] with a single energy dependent exponential decay length $\lambda(E)\sim c/E$. The layer based local densities of states for the β_2-(2×4) and (4×2) reconstructions are obtained from density-functional theory (DFT) calculations, in the local-density approximation (LDA), using norm-conserving pseudopotentials,[14,15] and the computer code FHI98MD.[16] Details of the calculation are reported in Ref. 9.

The local density of states for the first three layers of the β_2-(2×4), and ζ-(4×2) reconstructions are shown in Fig. 2. The results for the β_2-(4×2) reconstruction show only subtle differences with respect to the ζ-(4×2) reconstruction, for the reasons described above, and are not displayed here. The calculated work function, defined as the difference in electrostatic energy of the vacuum region from the Fermi energy, is ~5 eV, and is independent of the reconstruction in these calculations of the ideally reconstructed, unpinned, surfaces. We show only the energy region accessible to our experiment, extending ~5 eV below the Fermi energy. Two important points can be made in reference to Fig. 2. First, the second and third layer contributions to the LDOS are similar for both reconstructions and are bulk-like for the third layers.[17] Second, the ζ-(4×2) surface layer LDOS is substantially larger than that for the β_2-(2×4). Within the framework of our model, this would lead to an enhanced photoyield from the ζ-(4×2) reconstruction, in agreement with our experimental observations. In order for initial states, which are localized to the surface, to produce a measurable change in the photoyield, the electron escape depth must be at most on the order of 10 monolayers (~30 Å). This is reasonable given that the electron kinetic energies in our experiment are 5–10 eV.

In Fig. 3(a) the experimental monochromatized PE spectra of the As-stabilized (2×4) and In-stabilized (4×2) reconstructions are compared. The signal to noise ratio in the

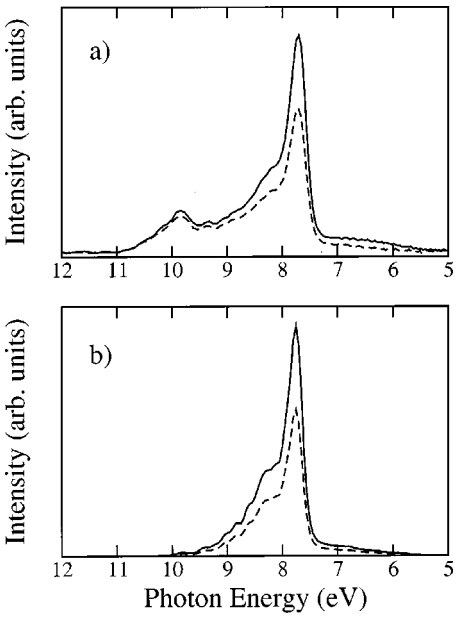

FIG. 3. (a) Measured PE yield from InAs (001) at 485 °C as a function of wavelength for the In terminated (4×2) (solid line) and the As terminated (2×4) (dashed line) reconstruction. (b) Calculated LDOS for InAs (001) convolved with D_2 lamp spectrum: ζ-(4×2), solid curve, $\beta 2$-(2×4), dashed curve.

threshold region of these spectra precludes any conclusive identification of threshold differences between the two reconstructions. The data do show that there is a marked increase in the photoelectron yield for the In terminated surface with respect to the As terminated one. In Fig. 3(b) the simulated photoelectron yield spectrum obtained by convolving the local density of states for the two reconstructions with the measured D_2 lamp spectrum is displayed. The differences in calculated spectra, approximately 10% total variation distributed over the range of the lamp spectrum, are in excellent agreement with the experimental trends. The discrepancy between measured and calculated spectra at 10 eV is due to a short wavelength cutoff in the measurement of the lamp spectrum used in the theoretical calculation.

This work is an important step in the development of an *in situ* sensor, which can be correlated, to morphological development on a semiconductor layer, which is subsequently processed into a device. We have shown that threshold PE can be used to monitor the development of surface morphological features *in situ* and in real time during MBE growth. A semiempirical model has been developed which correctly reproduces the measured PE yield trends from the stable reconstructions, establishing a basis for the interpretation of the photoyield trends, which we observe.

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